**Fundamental Role of Oxygen Stoichiometry in Controlling the Band Gap and Reactivity of Cupric Oxide Nanosheets**

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Supporting Information

**ABSTRACT:** CuO is a nonhazardous, earth-abundant material that has exciting potential for use in solar cells, photocatalysis, and other optoelectronic applications. While progress has been made on the characterization of properties and reactivity of CuO, there remains significant controversy on how to control the precise band gap by tuning conditions of synthetic methods. Here, we combine experimental and theoretical methods to address the origin of the wide distribution of reported band gaps for CuO nanosheets. We establish reaction conditions to control the band gap and reactivity via a high-temperature treatment in an oxygen-rich environment. SEM, TEM, XRD, and BET physisorption reveals little to no change in nanostructure, crystal structure, or surface area. In contrast, UV-vis spectroscopy shows a modulation in the material band gap over a range of 330 meV. A similar trend is found in H₂ temperature-programmed reduction where peak H₂ consumption decreases with temperature. Calculations of the density of states show that increasing the oxygen to copper coverage ratio of the surface accounts for most of the observed changes in the band gap. An oxygen exchange mechanism, supported by ¹⁸O₂ temperature-programmed oxidation, is proposed to be responsible for changes in the CuO nanosheet oxygen to copper stoichiometry. The changes induced by oxygen depletion/deposition serve to explain discrepancies in the band gap of CuO, as reported in the literature, as well as dramatic differences in catalytic performance.

Cupric oxide (CuO) is a p-type semiconductor that has been the subject of growing interest recently in the solar community as well as other fields including batteries, sensors, catalysis, supercapacitors, and others. In solar cells, CuO nanorod arrays have been used as an anode with TiO₂, as a barrier layer with ZnO, and as an active layer with C₆₀. Rajeshwar et al. found that differently synthesized CuO–C₆₀ nanorod arrays could photoelectrocatalytically convert CO₂ to methanol. Though it was also found that the different synthesis conditions led to different efficiencies, it is still unclear what material properties led to these observed differences in performance.

Though much work has been done using CuO for specific applications, basic material properties remain poorly defined, most prominently band gap. The band gap of bulk copper oxide has been reported to be between 1.2 and 2.1 eV. Additional inconsistencies exist between experimental results and theoretical models as to whether the transition is

Received: May 24, 2016

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DOI: 10.1021/jacs.6b05332

J. Am. Chem. Soc. XXXX, XXX, XXX–XXX
129 FMA-A2404, FMA-A2402-SS, and FMA5504 mass.

Oxidative and Inert Heat Treatment.

119 solution were added to the beaker, 3.4 g of copper(II) nitrate trihydrate was added to 100 mL of water and heated to 60°C. All gases used were ultrahigh purity obtained from Airgas.

Experimental Section.

In this work, CuO nanosheets were synthesized via a simple method with water as the reducing agent and argon as the inert gas. The reaction was initiated by dissolving cupric nitrate in water and then adding copper(II) nitrate trihydrate to the solution. The mixture was then heated to 60°C. The purity of the final product was confirmed by X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX).

METHODS

107 studies. Much research has been done on 0D and 1D materials, but there are only a few reports that discuss tuning the properties of 2D materials beyond graphene systems.

In this work, CuO nanosheets were synthesized via a simple surfactant-assisted aqueous-phase method and then annealed at 350°C in oxygen for different amounts of time. This annealing process was found to allow for the fine-tuning of the material's band gap as well as inimbing it with an increased reactivity. Theoretical tight-binding calculations show that oxygen coverage and arrangement strongly influence much of the band gap. A mechanism is finally proposed for this nondegradative process and supported with evidence from isotopic oxygen studies.

108 Experimental Section. All chemicals used here were purchased from Sigma-Aldrich with purity ≥ 97.7%. All gases used were ultrahigh purity obtained from Airgas.

109 Synthesis of Cupric Oxide Nanosheets. Cupric oxide nanosheets were synthesized as per the following protocol:

First, 120 g of sodium hydroxide and 22 g of hexadecyltrimethylammonium bromide (CTAB) were dissolved in 900 mL of deionized water and heated to 60°C under magnetic stirring. In a separate beaker, 3.4 g of copper(II) nitrate trihydrate was added to 100 mL of deionized water. Once dissolved, the contents of the copper nitrate solution were added to the first solution such that the final concentration of all species were 3 M NaOH, 60 mM CTAB, and 14 mM Cu(NO₃)₂, respectively. The solution was heated at a constant temperature of 60°C for 1 h and then removed from heating and filtered. The black precipitate was washed with excess deionized water and ethanol. To remove any remaining CTAB, the samples were then calcined at 250°C in air for 3 h and then finely ground with mortar and pestle before further treatment or characterization.

112 Oxidative and Inert Heat Treatment. The properties of cupric oxide nanosheets were tuned using a flow reactor as follows. Column-sized powders were dispersed in ethanol via sonication and then added dropwise to a holey carbon-coated gold grid. In both cases multiple spots were examined to ensure sample uniformity, and the EDX spectrum was acquired to verify that the structures were indeed composed of copper and oxygen.

113 X-ray Diffraction (XRD). XRD measurements were carried out on powder samples. Spectra were acquired from a Rigaku SmartLab X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) with a rotating anode source, operated at 45 kV and 200 mA. High-angle X-ray diffraction analysis software was used to obtain lattice constants and crystallite sizes.

114 UV–Visible Spectroscopy (UV–vis). UV–vis spectra were collected from an Applied NanoFluorence, LLC model NS1 Nanospectralizer. Samples were sonicated in water until dispersed and then circulated through a visible transparent cuvette. Measurements were repeated three to five times per sample, and then a Tauc plot was used to determine band gap. A software package was developed in house to automate this process as well as to improve interpretation consistency. The band gaps presented are the averages of the three to five samples, and the error bars represent the standard deviation of the measurements.

115 BET Surface Area. The surface area of CuO nanosheet samples was determined using a Quantachrome Autosorb. Adsorption–desorption isotherms were constructed using an 11-point Brunauer, Emmett, and Teller (BET) measurements protocol with N₂ as the adsorbate. Typically 50–100 mg of sample was used and outgassed at 200°C for 3–6 h. Measurements of each sample were performed in triplicate and their average and standard deviation calculated.

116 H₂ Temperature-Programmed Reduction (TPR) and ¹⁸O₂ Temperature-Programmed Oxidation (TPO). The TPR and isotopic oxygen studies were carried out in a reactor setup similar to that used for the TPO treatments with the addition of a sampling line at the outlet leading to a vacuum chamber operating at 10⁻⁸ to 10⁻⁷ Torr containing a SRS RGA 100 residual gas analyzer which was used to perform real-time mass spectrometry measurements. For TPR, 50 mg of sample was loaded into a straight tube quartz reactor, and a gas stream composed of 10% H₂ gas (90% Argon) was flowed over it at a rate of 100 mL/min for 1 h prior to heating. Flow rates were controlled using mass flow controllers. Samples were then heated from room temperature to 100°C in 5 min and then allowed to sit at 100°C for 5 min before ramping from 100 to 400°C at a rate of 10°C per minute. For TPO, 100 mg of CuO nanosheets was loaded, and a gas stream composed of 4% ¹⁸O₂ (96% He) was flowed over the sample. The purity of the ¹⁸O with respect to ¹⁶O was reported as 99:1. The sample was then heated to 450°C at a rate consistent with the TPR method. Again, the outlet gas was measured using the residual gas analyzer.

Computational. The structure of monoclinic CuO was generated from a unit cell found in the literature with a = 18.612 Å, b = 20.13, 16.40 Å, and c = 25.01 Å with α = 90.000°, β = 99.481°, and γ = 201°. The properties of cupric oxide nanosheets were tuned using a flow reactor as follows. Column-sized powders were dispersed in ethanol via sonication and then added dropwise to a holey carbon-coated gold grid. In both cases multiple spots were examined to ensure sample uniformity, and the EDX spectrum was acquired to verify that the structures were indeed composed of copper and oxygen.

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Figure 1. TEM (a) and SEM (b) images of untreated CuO nanosheets accompanied by EDX spectra (c) detailing its composition (copper and oxygen). The C and Al peaks are present because carbon tape was used to adhere powder samples to an aluminum stage. SEM images of 30, 60, and 120 min treated samples are presented in (d), (e), and (f), respectively.

![Image](image_url)

Figure 2. XRD spectra of CuO nanosheet 30 min (blue), 60 min (green), and 120 min (purple) treated and untreated (red) samples. Each peak is labeled with its corresponding face.

Cu and 32 O, resulting in a 6 nm thick slab. This structure is neutral, but each removed oxygen or copper atom increases the charge by 2 units or decreases the charge by 2 units, respectively. The long c lattice vectors act to install a spacer of about 17 Å to prevent unrealistic interactions between replicated slabs. The tight-binding extended Hückel Hamiltonian (EH) was chosen for its ability to model electronic structure, which for cupric oxide is monoclinic. This makes it possible to determine the oxidation state and overall composition of the sample to the stage and since this method is not sensitive enough to differentiate between the energies of carbon and oxygen, other methods (e.g., XRD) were used to confirm the material is in fact cupric oxide.

RESULTS AND DISCUSSION

Imaging. After synthesis, all samples were imaged to determine their nanostructure. Figures 1a and 1b show a typical TEM and SEM image (respectively) of an untreated sample. Here, we see that the material is in the form of nanosheets whose dimension ranges from 250 to 1000 nm in length and width. In previous work, we have found the nanosheet range in thickness between 15 and 25 nm. Also of note is the nonuniformity in the edges of the nanosheets, which others have cited as a result of the nanosheet growth process.

An EDX spectrum in Figure 1c provides elemental analysis of a structure found in the untreated sample and confirms it contains copper. Since carbon tape was used to adhere the sample to the stage and since this method is not sensitive enough to differentiate between the energies of carbon and oxygen, other methods (e.g., XRD) were used to confirm the material is in fact cupric oxide.

Figures 1d, 1e, and 1f show samples of copper oxide nanosheets after 30, 60, and 120 min of heat treatment at 350 °C, respectively. Here, we see that the nanosheet structure remains largely intact. Minor perturbations in the structure are, however, observable. For example, for the 120 min treated sample, there appears to be a rounding of the normally jagged edges present in the untreated sample. Indeed, for longer treatment times or for higher temperatures more extreme structural changes have been observed to occur (Figure S1). The temperature of 350 °C was chosen for this study because at higher temperatures structure loss was observed to occur too quickly.

Crystal Structure. X-ray diffraction (XRD) was used to determine the oxidation state and overall composition of the samples. Copper has two oxides: cuprous oxide (Cu2O) with copper having a +1 oxidation state and cupric oxide (CuO) in which copper has a +2 oxidation state. Fortunately each of these oxidation states has exactly one associated crystal structure, which for cupric oxide is monoclinic. This makes it possible to use XRD to determine the oxidation state of the copper in the samples.
XRD is an ideal technique for differentiating between samples of cupric and cuprous oxide. Figure 2 shows XRD spectra collected for treated and untreated samples. Peaks corresponding to each crystal face are labeled in Figure 2, and the lattice parameters of each are presented in Table 1.

<table>
<thead>
<tr>
<th>time treated (min)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (deg)</th>
<th>crystallite size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>4.6921</td>
<td>3.4287</td>
<td>5.1380</td>
<td>99.54</td>
<td>223 ± 28</td>
</tr>
<tr>
<td>30</td>
<td>6.6925</td>
<td>3.4275</td>
<td>5.1395</td>
<td>99.57</td>
<td>192 ± 62</td>
</tr>
<tr>
<td>60</td>
<td>6.6947</td>
<td>3.4276</td>
<td>5.1385</td>
<td>99.50</td>
<td>181 ± 51</td>
</tr>
<tr>
<td>120</td>
<td>6.6936</td>
<td>3.4218</td>
<td>5.1406</td>
<td>99.44</td>
<td>181 ± 56</td>
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</table>

Lattice constants were found to be approximately 4.69, 3.43, and 5.14 Å for a, b, and c, respectively, and approximately 95° for β (α = γ = 90°). The crystallite size was found to be approximately 200 Å which agrees with our previous studies. As well as empirical thickness calculations derived from surface area (vide infra).

The lattice parameter values agree well with literature values of CuO, and little change was observed for these values as a function of treatment time, which would suggest that the oxidative treatment has little to no effect on crystal structure or on the overall oxidation state. No cuprous oxide was detected in any sample.

Also of note is the increased amplitude of the peak associated with the (002) plane with respect to the other peaks compared to bulk (non-nano) CuO, which suggests an overexpression of the (002) plane in these CuO nanosheet samples, which other researchers have noted exhibits increased catalytic performance in the case of CO oxidation. The high reactivity of this plane may leave it more susceptible to alterations such as by introducing or annealing away defects or by functionalization of its surface. Below, we will demonstrate how changes to the surface of CuO nanosheets lead to differences in optical properties and reactivity.

Optical Properties. UV—visible spectroscopy was used to test differences in the optical properties of the CuO nanosheet samples. This technique has been extensively implemented in semiconductor research to determine a material’s band gap. Here, absorbance spectra of CuO nanosheets dispersed in deionized water were collected and plotted as a function of wavelength, which were then converted into Tauc plots via the following transformation

\[
(hvα)^{1/α} = A(hν - E_g)
\]

where h is Planck’s constant; ν is the frequency of light; α is the absorption coefficient; n = 1/2 for a direct band gap transition and 2 for an indirect band gap transition; A is a proportionality constant; and \(E_g\) is band gap. The band gap of a material may be determined by constructing a Tauc plot, that is by plotting \((αE_{\text{ph}})^{2}\) against \(E_{\text{ph}}\), where \(E_{\text{ph}}\) is the energy of a photon (hν). Linear extrapolation of each sample’s trace down to the \(E_{\text{ph}}\) axis should yield the value of the band gap of the materials.

Software was developed in-house to automate this process and to increase the consistency of the band gap determined for a given data set.

Example Tauc plots of each treatment are depicted in Figure S2, and calculated band gaps for each sample are plotted in Figure 3 as a function of treatment time. It was found that CuO nanosheets exhibit a direct band gap transition of 1.53 eV in the untreated sample. It was subsequently found that 30 min of oxidative treatment increased the band gap to 1.75 eV and 60 min to 1.86 eV. However, after 120 min of treatment, the band gap started to once again decrease, down to 1.82 eV. The standard deviations for all of these measurements were between 26 and 74 meV.

A separate sample of CuO nanosheets was treated at 350 °C for 30, 60, and 120 min in N₂ gas. Under these inert treatment conditions we observe a much smaller change in the band gap from 1.68 to 1.71 eV for untreated, 30, 60, and 120 min samples, respectively. We posit that the oxidative treatment results in more pronounced band gap changes due to increased O:Cu coverage of the CuO nanosheet surface. During inert treatment, no oxygen addition is possible from the gas phase though small band gap changes may be a result of oxygen and/or copper rearrangement from atoms already present on the surface. We also observe batch to batch differences in the band gap for untreated CuO nanosheets. In Figure 2, the untreated sample in the oxidative and inert series has a band gap of 1.53 and 1.68 eV, respectively, which we also attribute to a difference in the amount and distribution of surface oxygen atoms. Below, we use theoretical calculations in conjunction with experimental results to support these assertions as well as to demonstrate how differences to surface oxygen sites influence reducibility.

Theoretical Calculations. We have modeled the crystallographic structure of CuO, using tight-binding methods as described in the Computational methods section, to explore how the oxidative treatment changes the sample at a molecular level. Figure 4 shows the total density of states (DOS) for model 2D CuO nanosheets as well as the projected density of states (PDOS) for Cu and O atoms. For an ideal CuO structure with 1:1 ratio of Cu:O (Figure 4a), the band gap is 1.05 eV, in reasonable agreement with other theoretical calculations and acceptably close to the band gap value found in Table 2 for the untreated sample. Typically, band gaps obtained at this level of theory underestimate the experimental band gaps by a few 100 meV. To simulate an oxygen-rich surface, 8, 16, and 24 Cu atoms were removed from the top layer, as shown in Figures 4b, 4c, and 4d, respectively. Cu depletion resulted in a band gap increase, from 1.05 to 1.26 eV and 1.42 and 1.75 eV for the 0, 8, 16, and 24 Cu atoms removed, respectively. Conversely

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<table>
<thead>
<tr>
<th>Band gap (eV)</th>
<th>Oxidative treatment</th>
<th>Inert treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>1.53</td>
<td>1.68</td>
</tr>
<tr>
<td>30 min</td>
<td>1.75</td>
<td>1.82</td>
</tr>
<tr>
<td>60 min</td>
<td>1.86</td>
<td>1.82</td>
</tr>
<tr>
<td>120 min</td>
<td>1.71</td>
<td>1.82</td>
</tr>
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</table>

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Table 1. Lattice Parameters and Crystallite Sizes for the CuO Nanosheets in Figure 2

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Figure 3. Band gaps of treated and untreated CuO nanosheet samples in an oxidative treatment (red solid) and with an inert treatment (black dotted). Each data point is an average over five measurements, and the error bars represent the standard deviation.
removing oxygen atoms from the bottom layer (Figure S3) resulted in a band gap decrease from 1.05 to 0.57 eV for 0 to 24 O atoms removed. These results are summarized in Table 3 and the Supporting Information. We find that changes in the band gap largely result from a change in the conduction band of the material, rich in Cu d states, increasing in the case of Cu removal and decreasing in the case of O removal. The results of our theoretical models are consistent with the experimental conclusion that the band gap of CuO increases with increasing surface oxygen coverage. It is expected that the surface of CuO nanosheets becomes relatively more oxygen rich when exposed to the oxidative treatment, which is consistent with the observed increase in band gap. Similar results were obtained for CuO nanowires where adsorption of water to the (111) surface resulted in a wider band gap.56

The rearrangement of oxygen on the surface was also investigated using molecular modeling to determine its impact on the CuO nanosheet band gap. Such calculations effectively model the effect of surface rearrangement upon oxidation or reduction. In Figure 5a, 16 Cu atoms were removed from the bottom layer, but the pattern of removal was varied. In Figure 5a, the atoms were removed in a regular fashion, that is, the first atom of the first vertical row, the second atom of the second row, etc. In (b) adjacent rows of Cu atoms were deleted. In (c) alternating rows were deleted. "Areas" (d) refer to roughly hexagonal portions deleted from the surface. Color code: blue = Cu, red = O.

![Figure 4](image-url)  
*Figure 4. Total DOS (black) and pDOS (blue = Cu, red = O) for CuO (geometries shown as in insets) in various states of removal from the top copper layer in a “regular” fashion where the first atom is deleted in the first vertical row, the second atom is deleted in the second vertical row, etc. The pristine slab is given in (a). 8, 16, and 24 Cu atoms are deleted in (b), (c), and (d), respectively. Color code: blue = Cu, red = O.*

![Figure 5](image-url)  
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<table>
<thead>
<tr>
<th>Table 2. Mean Values for the Band Gap of Each CuO Nanosheet Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>time treated (min)</td>
</tr>
<tr>
<td>untreated</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>120</td>
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</table>

<table>
<thead>
<tr>
<th>Table 3. Values for the Band Gap of Each CuO Model Given in Figures 4 and 5</th>
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</thead>
<tbody>
<tr>
<td>Cu atoms removed</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>16</td>
</tr>
<tr>
<td>16</td>
</tr>
<tr>
<td>16</td>
</tr>
<tr>
<td>16</td>
</tr>
<tr>
<td>24</td>
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These theoretical results also help explain changes found in CuO nanosheets treated in an inert environment. Slight increases and decreases in band gap found can be attributed to the rearrangement of oxygen atoms on the surface. For example, structures may transition from a “regular” distribution to an “alternating” arrangement, which would increase the band gap, then to an “adjacent” configuration, which would decrease the band gap, or to the “areas” structure, which would keep the band gap relatively constant. Based on the experimental results the latter is more likely since little to no change in band gap is observed.

Reactivity. In this section, we demonstrate how increases in the band gap of CuO nanosheets correlate with increases in reactivity. Hydrogen oxidation was used as a probe reaction to quantify differences in reducibility. The reduction of CuO in hydrogen gas is a well-studied process,\textsuperscript{43} CuO, rather than being reduced sequentially to Cu₂O and then to Cu, has been shown to reduce directly to Cu according to the following reaction:

\[ \text{CuO(s)} + \text{H}_2(g) \rightarrow \text{Cu(s)} + \text{H}_2\text{O}(g) \]

First, the surface areas of all samples were measured in triplicate using 11 point BET N\textsubscript{2} physisorption. The mean of each sample along with the standard deviation is listed in Table 4. All samples fell within a range of 20–24 m\textsuperscript{2}/g with very little difference in surface area between them. Interestingly, surface area can be used to calculate the average thickness of the nanosheets present within the sample using eq 2.

\[ \bar{t} = \frac{2}{\rho} \]  

where \( \bar{t} \) is the average thickness of a CuO nanosheet; \( \sigma \) is the surface area per unit mass of the sample; and \( \rho \) is the density of CuO, which is 6.31 × 10\textsuperscript{3} g/m\textsuperscript{3}. An analogue analysis is done by Weiber et al. for 0D nanoparticles;\textsuperscript{57} however, since no such report exists for 2D materials (to the best of our knowledge) a short derivation is included in the Supporting Information, Section II.

Thicknesses for each sample are presented in Table 4. These values were likely an underestimation of the actual thickness since roughness and jagged edges, which are visible from the SEM images in Figure 1, increase the surface area. Interestingly these values are in agreement with crystallite sizes obtained from XRD. Together with the SEM images shown in Figure 1, these data reinforce the claim that the treatment has not impacted the structure of the CuO nanosheets.

H\textsubscript{2} TPR was performed on oxidized CuO nanosheets, as shown in Figure 6. Here 50 mg of treated and untreated samples were heated in 10% H\textsubscript{2} gas (in an Ar atmosphere) flow from 100 to 400 °C, and the composition of the outlet gas stream was assessed using mass spectrometry. Since no gaseous oxygen is present for this reaction, all hydrogen that is consumed is being oxidized by the CuO nanosheets, which degrades the CuO nanosheets so that neither structure nor composition is preserved. However, differences in the initial state of the nanosheets affect the temperature at which the material reacts.

Percent H\textsubscript{2} consumption is given as a function of temperature in Figure 6 for each sample. At a given temperature, increased H\textsubscript{2} consumption indicates more reaction is occurring between the material and the gas. When all of the oxygen has been depleted (i.e., when all CuO has been converted to Cu) the reaction ceases, and no further H\textsubscript{2} is consumed. In Figure 6, we see that peak H\textsubscript{2} consumption temperature decreases from 261 °C for the untreated sample to 242 °C for the 30 min treated sample and to 214 °C for the 60 min treated sample. For the 120 min sample, the peak H\textsubscript{2} consumption temperature increases back to 244 °C. Note that this follows a similar trend to the sample's band gap in that CuO nanosheets with higher band gap show increased reactivity with H\textsubscript{2} (as indicated by a lower reaction temperature) and vice versa, which indicates that there is a correlation between the band gap and reactivity of CuO nanosheets so that by tuning one the other is also tuned, which makes it possible to predict a priori how changes in the band gap of CuO nanosheets will impact its reactivity.

Values for total H\textsubscript{2} consumed are listed in Table 5. These values were derived by integrating the H\textsubscript{2} consumption curves and using the prior knowledge of the quantity of H\textsubscript{2} flowed during the experiment. Equation 3 outlines this explicitly.

\[ \frac{\text{Peak Area}}{\text{Total Area}} = \frac{\text{H}_2 \text{Consumed}}{\text{Total H}_2 \text{Flowed}} \]  

Table 5. Peak Consumption Temperatures\textsuperscript{a}

<table>
<thead>
<tr>
<th>time treated (min)</th>
<th>peak H\textsubscript{2} consumption temp. (°C)</th>
<th>total H\textsubscript{2} consumed (mmol)</th>
<th>Cu:O</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>261</td>
<td>0.794</td>
<td>1:1.26</td>
</tr>
<tr>
<td>30</td>
<td>242</td>
<td>0.761</td>
<td>1:1.21</td>
</tr>
<tr>
<td>60</td>
<td>214</td>
<td>0.777</td>
<td>1:1.23</td>
</tr>
<tr>
<td>120</td>
<td>244</td>
<td>0.775</td>
<td>1:1.24</td>
</tr>
</tbody>
</table>

\textsuperscript{a}These temperatures follow a trend similar to the material band gap. Total H\textsubscript{2} consumed was found by integrating each peak and using the ideal gas law. Cu:O ratios were determined assuming 1 mol of H\textsubscript{2} per atom of O present in the material.
where Total Area is the area below the line $y = 100\%$ from 100 to 400 °C or $100 \times 300 = 30,000$ which is the theoretical maximum consumption. The total H$_2$ flowed refers the total amount of moles calculated using a flow rate of 10 mL/min (10% of a 100 mL/min stream) and the ideal gas law. From the above reaction, 1 molecule of H$_2$ is consumed per oxygen atom of CuO. Therefore, these values also serve as a measure of oxygen content for these structures. The theoretical amount of O atoms in 50 mg of sample with a 1:1 Cu:O ratio is 0.630 mmol. In this study we find that all CuO nanosheet samples had increased amounts of oxygen. As depicted in Table 4 the Cu:O ratio goes from 1:1.26 in the untreated sample to 1:1.21 to 1:1.24 to 1:2.3. Thus, all CuO nanosheets studied here have an excess amount of oxygen, which would explain why the band gaps do not match a theoretical pristine slab of CuO where the ratio for Cu:O is 1:1. This trend is not identical to the trend in band gap in that the untreated sample, though it contains the most oxygen, does not have the highest band gap. In the treated samples, however, the oxygen amount does follow the trend of band gap. Based on our theoretical calculations, we conclude that the surface oxygen atoms in the untreated sample are more dispersive than the treated samples, which corroborates the hypothesis made in the previous section that the solution synthesized CuO nanosheets exist in a different configuration, and with heat treatment these structures can rearrange, changing their band gap. More robust spectroscopic methods may reveal that the surface of untreated CuO nanosheets contains more hydroxyl groups that likely affect the band gap in different ways, as suggested in the literature, which is beyond the scope of this investigation.

H$_2$ TPR was also performed on a commercial sample of CuO, and it was found that it contained only 3.9% more oxygen (Figure S5). The high surface-to-bulk ratio of CuO nanosheets suggests that a large amount of additional oxygen lies on the surface of the material, which would explain why the band gaps reported in this work are slightly higher than the most commonly cited value of 1.4 eV.

To further support the hypothesis that oxygen from the gas phase is interacting with the material and vice versa, $^{18}$O$_2$ temperature-programmed oxidation was performed on untreated CuO nanosheets. Figure 7 shows the production of $^{18}$,16O$_2$ as a function of temperature over untreated CuO nanosheets. At approximately 325 °C there is an onset of production of $^{18}$,16O$_2$. Since the atmosphere is the only source of $^{18}$O atoms (in the form of $^{18}$O$_2$) and CuO nanosheets are the only source of $^{14}$O atoms, the production of $^{18}$,16O$_2$ molecules must be a result of oxygen exchange occurring between the nanosheets and the gas. This mechanism similar to Mars–Van Krevelen catalysts is indicative of increased oxygen mobility in the material. We posit that this phenomenon might also be the mechanism of structural degradation in nanosheet samples heated over long time periods around this temperature (Figure S1). Thus, we conclude that the band gap and reactivity changes are a direct result of this oxygen mobility and exchange.

In analogous systems, such as carbon nanotubes, surface oxygen groups impact properties such as toxicity, reactivity, and point of zero charge. Additionally, others have noted the correlation between band gap and catalytic performance in metal oxide systems. Here, we find that the total amount of surface oxygen as well as its distribution affect the band gap and hydrogen oxidation activity of CuO nanosheets. We also find that these optical and catalytic properties may be tuned through varying the calcination condition.

**CONCLUSIONS**

We have elucidated the fundamental role that surface oxygen deposition plays in tuning the band gap and reactivity of CuO nanosheets, an earth-abundant, nonhazardous material, useful in the fields of solar energy technology and photocatalysis. We demonstrated that the band gap of CuO nanosheets can be controlled in a range of 1.53–1.86 eV through a mild oxidative heat treatment. We found that the reactivity of the nanosheets improves upon increasing the band gap, as evidenced by H$_2$ TPR. The observed changes in band gap and reactivity are directly correlated with changes in surface oxygen coverage, as supported by our theoretical analysis. Calculations of the DOS for a series of model CuO nanosheets show that structures with increased surface oxygen atoms have larger band gaps. Additionally, the band gaps of models with more ordered arrangements varied widely from those of more diffuse arrangements. Finally, through isotopic oxygen TPO, we demonstrate that oxygen exchange is indeed occurring between the gas phase and the solid during the oxidative heat treatments at 350 °C. We hypothesize that the sensitivity to surface oxygen vacancies is an important contributing factor for the wide range of values of CuO band gaps reported in the literature.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05332.

**SEM image showing the effects that long heat treatments have on CuO nanosheets, namely, that nanostructure degradation begins with the smoothing of the material’s jagged edges, mass spectrometry data for H$_2$ TPR of commercial CuO showing the percent of H$_2$ consumed at any given temperature, derivation of eq 2, and coordinates for structures used for the theoretical calculations (PDF)**

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**Notes**

The authors declare no competing financial interest.
HEEDSTROM for their advice on the theoretical calculations.

ACKNOWLEDGMENTS

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